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(54) **Motion picture film having improved protective overcoat and protective backcoat**

(57) A motion picture print film comprising a support having on one side thereof at least one silver halide emulsion layer and an outermost protective overcoat layer comprising a film-forming binder, and having on the opposite side thereof an outermost protective backcoat layer comprising a film-forming binder; wherein the protective overcoat and backcoat layers each comprise at least 1 mg/m² of permanent matting agent having an average size of from 0.5 to 3 micrometers, the total permanent matting agent amount in the overcoat and back-

coat layers combined is less than 25 mg/m², at least one of the overcoat or backcoat layers comprises soluble matting agent having an average size of from 0.5 to 3 micrometers which is removed upon photographic processing, and the total soluble matte amount in the overcoat and backcoat layers combined is from 2.5 to 30 mg/m². Print films in accordance with the invention simultaneously give excellent protection from ferrotyping, improved resistance to the generation of dirt and abrasion, and excellent image quality and soundtrack reproduction.

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Description

[0001] The present invention relates in general to photography and in particular to a novel photographic element that is especially useful as a motion picture print film. More specifically, this invention relates to a motion picture print film having protective overcoat and backcoat layers which comprise permanent matting agent and at least one of the overcoat or backcoat comprises removable matting agent.

[0002] Motion picture print films, the film that is shown in movie theaters, commonly employ optical sound tracks along at least one edge of the film. The most common optical sound tracks presently in use are analog sound tracks of the "variable area" type wherein signals are recorded in the form of a varying ratio of opaque to relatively clear area along the sound track. During projection of the motion picture images, a light source illuminates the sound track and a photosensor senses the light passing through and modulated by the sound track to produce an audio signal that is sent to amplifiers of the theater sound system. Digital sound tracks for motion picture films have been more recently introduced, wherein sound information is recorded in a digital format, e.g. comprising small data bit patterns on the film, typically between perforations of the motion picture film (e.g., Dolby™ Digital Stereo sound tracks) or along the film edge (e.g., Sony™ Dynamic Digital Sound sound tracks).

[0003] In order to optimize the visual quality of the motion picture image as well as the sound quality of the sound track recorded on a motion picture print film, the motion picture and sound track are first typically captured or recorded on separate photosensitive films as negative images, and the resulting negatives are then printed in synchronization on the motion picture print film to form positive images. Because of very short exposure times which must be given to each separate picture, or frame, in capturing a motion picture image, a camera negative film employing relatively fast silver halide emulsions is typically used to record the motion picture images (e.g., Eastman Color Negative and Kodak Vision Color Negative films). In order to reproduce the wide ranges of colors and tones which may be found in various images, the camera film typically also has a relatively low contrast or gamma. Variable area analog sound tracks and digital sound tracks, however, are best recorded with high contrast, relatively slow speed black and white films (e.g., Eastman Sound Recording Films) in order to generate desired sharp images for the sound recording and minimize background noise generated by relatively high minimum densities typically associated with relatively fast films.

[0004] Sound performance is ultimately measured on the print film because that is the vehicle for transmitting the sound film information to the amplifiers in the theater. Common sound systems for reading analog sound tracks incorporate a photodiode in the projector. The photodiode's radiant sensitivity peaks at approximately 800-950 nm (depending on the photodiode type), allowing it to detect predominantly infra-red (IR) radiation emitted by common tungsten lamps. In order to provide effective modulation of common projector illumination light, the optical analog sound track is typically formed in a color motion picture print film by printing the sound track with green and red light to expose the green-and-red-light sensitive layers of the color print film, and then specially processing the optical analog sound track area of the print film differently from the picture image frame area such that a silver image is present in the sound track area of the film in addition to the formed magenta and cyan image dyes. The silver image has good detection in the IR, but the special treatment of the sound track area does add complexity to the photo-processing of the color print film. The photo-process is described in Kodak Publication No. H-24, The Kodak ECP-2B Process, Manual for Processing Eastman Color films, referenced above. Various other techniques are also known for retaining silver in the sound track area, e.g., as set forth in U.S. Patents 2,220,178; 2,341,508; 2,763,550; 3,243,295; 3,705,799; 4,139,382. In digital sound tracks, photo-processing of the print film yields dye images which are decoded in the theaters with either green or red readers. There are optimum print dye densities that correspond to sound negative silver densities that will enable the best possible sound performance. In many theaters, digital sound is preferred and analog sound serves as a backup, in the event that the digital sound track cannot be read.

[0005] Different metrics are employed to assess the performance of the various sound tracks. Performance of analog sound tracks is measured by a metric termed cross-modulation. Cross-modulation (X-mod) measures the ability of the image distortion, present as image spread, in the sound negative to be cancelled by the image spread in the print film. The closer to exact the cancellation, the truer the sound representation. Dolby Digital Stereo employs DQI (Dolby Quality Index) as the metric to assess the quality of Dolby sound on the print film. The performance rating is numerical from 0-100. A higher number is indicative of better performance. The performance rating system for Sony assigns a letter grade with A representing the best performance. All sound systems incorporate a variable dependent on image spread to rate the quality of the sound.

[0006] The incorporation of matting agents in the outermost layers of photographic elements is well known. These matting agents can reduce the potential for a photographic film to ferrotype when the backside of the film is in contact with the frontside (i.e., emulsion side) of the film under the pressures that are typical of, for example, a tightly wound roll of film. Ferrotyping may cause the two sides of the film to stick together, and, under severe cases of ferrotyping, damage to the emulsion side surface layer may occur when the roll is unwound.

In some cases, ferrotyping may have an adverse effect on the sensitometric response of the photographic emulsion. Matting agents are also employed for such purposes as reduction of static charging and excessive sheen, pencil mark

acceptance and avoidance of Newton's rings. A wide variety of materials have been employed as matting agents including both inorganic and polymeric fine particles as illustrated by Research Disclosure, Item 38957, pages 615-616, September, 1996.

[0007] Large quantities of matting agents are often employed for the purposes described above. However, the use of a large quantity of matting agent may result in undesirable side effects such as increased haze and graininess of the processed image. To overcome these limitations, a matting agent that is removed during film processing is often employed in place of "permanent" matting agents. Such "removable" or "soluble" matting agents are typically alkali soluble polymeric matte particles comprising, for example, a copolymer of methyl methacrylate and methacrylic acid. Soluble matte particles are described, for example, in U.S. Patent Nos. 2,322,037; 2,992,101; 3,767,448; 4,094,848; 4,142,894; 4,447,525 and 4,524,131. Because these matte particles are removed during film processing, they can generally be employed in the photographic film at high dried coating weights, for example, 200 mg/m² or more of matte particles. However, in some cases the use of large quantities of soluble matting agent may result in undesirable side effects. Soluble matte beads have a tendency to swell or dissolve during preparation, delivery, or coating of the solution containing the matte beads thus causing various types of coating defects in the film. During film processing, the removal of soluble matte beads may leave behind pits or craters in the coating, these may be visible especially under the very high magnifications typically used for viewing a motion picture print film, for example. The use of large quantities of soluble matting agent (as well as permanent matting agent) may generate a fine dust of particles due to the matting agent being dislodged from the unexposed and unprocessed film during film manufacture and use. The matte dust generated may become lodged on the photographic emulsion and cause image defects during subsequent exposure and film processing. In addition, these dislodged particles may scratch and abrade the photographic film.

[0008] Any matting agent (permanent or soluble) used in motion picture print films can potentially affect image quality and soundtrack reproduction during theater viewing. Large amounts of permanent or soluble matting agent present in a print film emulsion overcoat during printing of the print film from a duplicate negative will result in image graininess during projection. Even moderate amounts of permanent matting agent present on either side of the exposed and processed print film can effect image graininess during projection. Soundtrack reproduction quality (i.e., frequency response and signal-to-noise ratio) may be degraded at substantially lower matting agent levels than those necessary to affect image quality, this is especially true for those films that utilize a digital soundtrack.

[0009] A photographic element especially useful as a motion picture print film is described in U.S. Patent No. 5,679,505. This patent discloses a film comprised of a support having on one side an antihalation undercoat and at least one silver halide emulsion layer and having on the opposite side an antistatic layer and a protective topcoat comprised of a polyurethane binder. The topcoat includes from 1 to 100 mg/m², preferably from 15 to 65 mg/m², of matte beads. Examples in the '505 patent teach a topcoat having 30.7 mg/m² permanent matte and an emulsion overcoat having 5 mg/m² permanent matte. While the films described in this patent are shown to have resistance to scratch, abrasion and ferrotyping there is a need to further improve these properties while also improving soundtrack reproduction.

[0010] Thus while much prior art has been disclosed that relates to photographic elements having various types of matting agents, providing a motion picture print film that simultaneously gives excellent protection from ferrotyping, freedom from dirt and abrasion, and excellent image quality and soundtrack reproduction has proven to be a difficult challenge. It is therefore a general aim of the present invention to provide an improved motion picture print film that resists ferrotyping while avoiding the problems and limitations of the prior art. It is a further aim of the invention to provide a motion picture print film that has improved image quality and soundtrack reproduction during theater viewing. It is yet a further aim of the invention to provide a motion picture print film that has improved resistance to the generation of dirt and abrasion.

[0011] In accordance with the present invention there is provided an unprocessed motion picture print film comprising a support having on one side thereof at least one silver halide emulsion layer and an outermost protective overcoat layer comprising a film-forming binder, and having on the opposite side thereof an outermost protective backcoat layer comprising a film-forming binder; wherein the protective overcoat and backcoat layers each comprise at least 1 mg/m² of permanent matting agent having an average size of from 0.5 to 3 micrometers, the total permanent matting agent amount in the overcoat and backcoat layers combined is less than 25 mg/m², at least one of the overcoat or backcoat layers comprises soluble matting agent having an average size of from 0.5 to 3 micrometers which is removed upon photographic processing, and the total soluble matte amount in the overcoat and backcoat layers combined is from 2.5 to 30 mg/m².

[0012] Motion picture print film photographic elements of the invention comprising a support having on one side thereof at least one silver halide emulsion layer and an outermost protective overcoat layer, and having on the opposite side thereof an outermost protective backcoat layer. In preferred embodiments, the elements of the invention may include an antihalation undercoat between the support and the silver halide emulsion layer, and an antistatic layer on either side of the support.

[0013] The outermost protective overcoat and the outermost protective backcoat layers of the elements of the in-

vention comprise film-forming binder and matting agent. The use of film-forming hydrophilic colloids as binders in photographic elements, including photographic films and photographic papers, is very well known. The most commonly used of these is gelatin and gelatin is a particularly preferred material for use in the outermost layers of this invention. It can preferably be used as the binder in the protective overcoat, antihalation undercoat and in the silver halide emulsion layer(s). Useful gelatins include alkali-treated gelatin (cattle bone or hide gelatin), acid-treated gelatin (pigskin gelatin) and gelatin derivatives such as acetylated gelatin, phthalated gelatin and the like. Other hydrophilic colloids that can be utilized alone or in combination with gelatin include dextran, gum arabic, zein, casein, pectin, collagen derivatives, collodion, agar-agar, arrowroot, albumin, and the like. Still other useful hydrophilic colloids are water-soluble polyvinyl compounds such as polyvinyl alcohol, polyacrylamide, poly(vinylpyrrolidone), and the like.

[0014] The film-forming binder useful in the protective backcoat of the invention can be essentially any known polymeric binder. This includes the abovementioned hydrophilic colloids as well as hydrophobic polymers. Useful hydrophobic polymers include polyurethanes, polyesters, polyamides, polycarbonates, cellulose esters, acrylic polymers, styrenic polymers, and the like. Particularly preferred polymeric binders for use in the backcoat of the invention include aliphatic polyurethanes such as those described in U.S. Patent No. 5,679,505.

[0015] In practice of the present invention the protective overcoat and the backcoat each comprise at least 1 mg/m² of permanent matting agent having an average size of from 0.5 to 3 micrometers, the total permanent matte amount in the overcoat and backcoat combined is less than 25 mg/m², at least one of the overcoat or backcoat comprises soluble matting agent having an average size of from 0.5 to 3 microns, and the total soluble matte amount in the overcoat and backcoat combined is from 2.5 to 30 mg/m². Preferably, the soluble matting agent in at least one of the overcoat or backcoat layers is present at a level at least equal to that of the permanent matting agent, such that the average roughness (ASME B46.1-1995) for the overcoat or backcoat is substantially higher prior to photographic processing than after photographic processing.

[0016] The requirement that the protective overcoat and backcoat each comprise at least 1 mg/m² of permanent matte insures good transport characteristics throughout the entire manufacturing process and use of the film. Also, a combined amount of permanent matte in the overcoat and backcoat that is less than 25 mg/m² insures very low haze which provides excellent soundtrack reproduction. A combined amount of soluble matte in the overcoat and backcoat that is from 2.5 to 30 mg/m² insures excellent ferrotyping protection for the unprocessed film while avoiding problems associated with the use of large quantities of soluble matte. Thus, these unique matting agent characteristics for the overcoat and backcoat for the motion picture print film of the present invention provide optimum performance throughout all stages of film manufacture, printing, and projection.

[0017] The permanent matting agent may be silica or other mineral oxides, calcium carbonate, glass spheres, ground polymers, or polymeric matte beads. Polymeric matte beads are preferred because of their uniformity of shape and uniformity of size distribution. The polymeric matte beads may be crosslinked or uncrosslinked. The surface of the polymeric matte beads may be attached to gelatin or other hydrophilic colloids to improve their dispersibility in aqueous media. The polymeric matte beads may be prepared by a limited coalescence process such as described in U.S. Patent Nos. 4,965,131 and 5,133,912.

[0018] The soluble matting agent may be any particulate material which is insoluble in water and soluble in aqueous alkali media. Particularly preferred soluble matting agents are polymeric matte beads that are copolymers of an alkyl methacrylate and methacrylic acid such as those described in U.S. Patent Nos. 2,992,101; 3,767,448; 4,142,894 and 4,447,525.

[0019] In addition to film-forming binder and matting agents the protective overcoat and the protective backcoat of the invention may optionally contain surface active agents, antistatic agents, charge control agents, thickeners, ultra-violet light absorbers, processing removable dyes, high boiling point solvents, colloidal inorganic particles, magnetic recording particles, polymer latexes, crosslinking agents (i.e., hardeners) and lubricants. Useful lubricants include silicones, natural and synthetic waxes, stearates, amides, and perfluorinated polymer particles. The lubricants should be included to give the overcoat and the backcoat a coefficient of friction that ensures good transport characteristics and resistance to scratch and abrasion during manufacturing and customer use. For satisfactory transport characteristics the overcoat and backcoat should have a friction coefficient of from 0.1 to 0.4. However, the most preferred range is from 0.15 to 0.3. If the protective overcoat and backcoat coefficient of friction is below 0.15, there is a significant danger that long, slit rolls of the photographic film will become unstable in storage or shipping and become telescoped or dished, a condition common to unstable film rolls. If the coefficient of friction is above 0.30 at manufacture or becomes greater than 0.30 after photographic film processing, a common condition of non-process surviving protective overcoat lubricants, the photographic film transport characteristics become poorer, particularly in some types of photographic film printers and projectors.

[0020] The materials employed as the support member are synthetic high molecular weight polymeric materials. These materials may be comprised of various polymeric films, but polyester and cellulose triacetate film supports, which are well known in the art, are preferred. The thickness of the support is not critical. Conventional support member thicknesses of from 50 to 250 microns (2 to 10 mils, or 0.002 to 0.010 inches) can be employed, for example, with very

satisfactory results. Polyester support members typically employ a primer layer between the functional layers and the polyester support. Such primer layers are well known in the art and comprise, for example, a vinylidene chloride/methyl acrylate/itaconic acid terpolymer or vinylidene chloride/acrylonitrile/acrylic acid terpolymer as described in U.S. Patents 2,627,088; 2,698,235; 2,698,240; 2,943,937; 3,143,421; 3,201,249; 3,271,178 and 3,501,301.

[0021] The antihalation undercoat used in preferred embodiments of this invention functions to prevent light from being reflected into the silver halide emulsion layer(s) and thereby causing an undesired spreading of the image which is known as halation. Any of the filter dyes known to the photographic art can be used in the present invention as a means of reducing halation. Thus, for example, water-soluble dyes can be used for this purpose. Such dyes should be incorporated in the antihalation undercoat with a mordant to prevent dye diffusion. Alternatively, and preferably, a solid particle filter dye is incorporated in the antihalation undercoat.

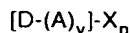
[0022] Useful water-soluble filter dyes for the purpose of this invention include the pyrazolone oxonol dyes of U.S. Patent 2,274,782, the solubilized diaryl azo dyes of U.S. Patent 2,956,879, the solubilized styryl and butadienyl dyes of U.S. Patents 3,423,207 and 3,384,487, the merocyanine dyes of U.S. Patent 2,527,583, the merocyanine and oxonol dyes of U.S. Patents 3,486,897; 3,652,284 and 3,718,472, the enamino hemioxonol dyes of U.S. Patent 3,976,661, the cyanomethyl sulfone-derived merocyanines of U.S. Patent 3,723,154, the thiazolidones, benzotriazoles, and thiazolothiazoles of U.S. Patents 2,739,888; 3,253,921; 3,250,617 and 2,739,971, the triazoles of U.S. Patent 3,004,896, and the hemioxonols of U.S. Patents 3,125,597 and 4,045,229. Useful mordants are described, for example, in U.S. Patents 3,282,699; 3,455,693; 3,438,779 and 3,795,519.

[0023] Preferred examples of solid particle filter dyes for use in antihalation undercoat layers include those which are substantially insoluble at aqueous coating pH's of less than 7, and readily soluble or decolorizable in aqueous photographic processing solutions at pH of 8 or above, so as to be removed from or decolorized in a photographic element upon photographic processing. By substantially insoluble is meant dyes having a solubility of less than 1% by weight, preferably less than 0.1 % by weight. Such dyes are generally of the formula:



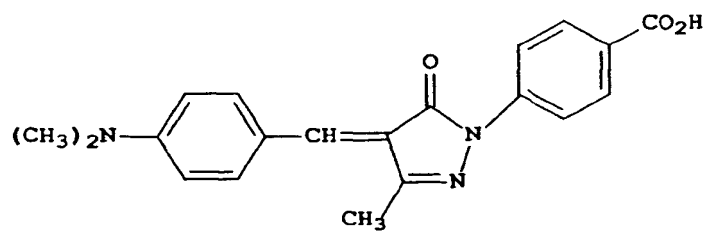
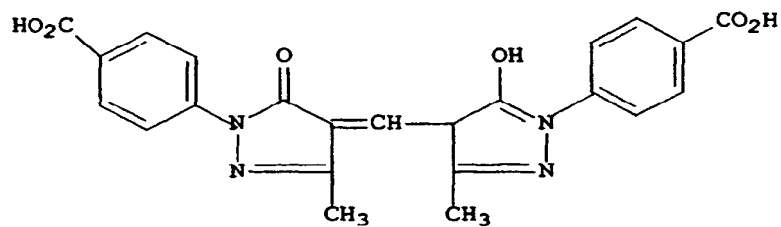
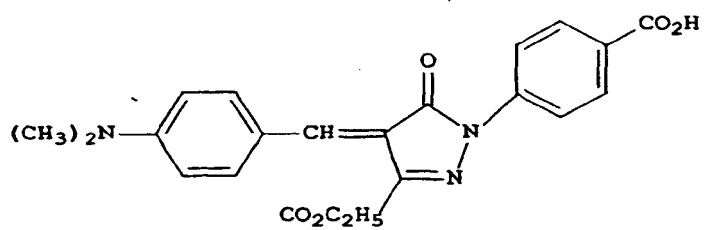
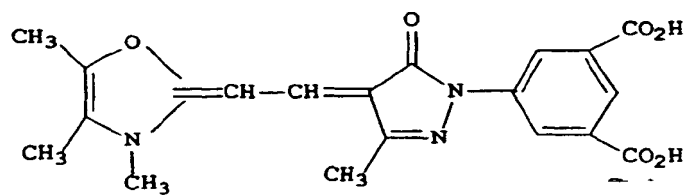
where D represents a residue of a substantially insoluble compound having a chromophoric group, X represents a group having an ionizable proton bonded to D either directly or through a bivalent bonding group, and n is 1-7. The residue of a compound having a chromophoric group may be selected from conventional dye classes, including, e.g., oxonol dyes, merocyanine dyes, cyanine dyes, arylidene dyes, azomethine dyes, triphenylmethane dyes, azo dyes, and anthraquinone dyes. The group having an ionizable proton preferably has a pKa (acid dissociation constant) value measured in a mixed solvent of water and ethanol at 1:1 volume ratio within the range of 4 to 11, and may be, e.g., a carboxyl group, a sulfonamido group, a sulfamoyl group, a sulfonylcarbonyl group, a carbonylsulfamoyl group, a hydroxy group, and the enol group of a oxonol dye or ammonium salts thereof. The filter dye should have a log P hydrophobicity parameter of from 0-6 in its non-ionized state. Such general class of ionizable filter dyes is well known in the photographic art, and includes, e.g., dyes disclosed for use in the form of aqueous solid particle dye dispersions as described in International Patent Publication WO 88/04794, European patent applications EP 594 973; EP 549 089; EP 546 163 and EP 430 180; U.S. Patents 4,803,150; 4,855,221; 4,857,446; 4,900,652; 4,900,653; 4,940,654; 4,948,717; 4,948,718; 4,950,586; 4,988,611; 4,994,356; 5,098,820; 5,213,956; 5,260,179 and 5,266,454. Such dyes are generally described as being insoluble in aqueous solutions at pH below 7, and readily soluble or decolorizable in aqueous photographic processing solutions at pH 8 or above.

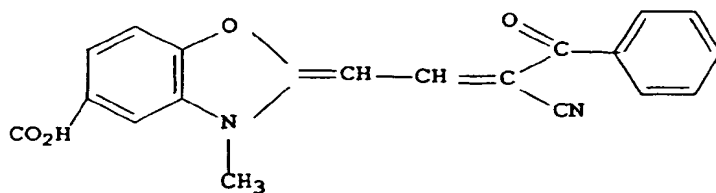
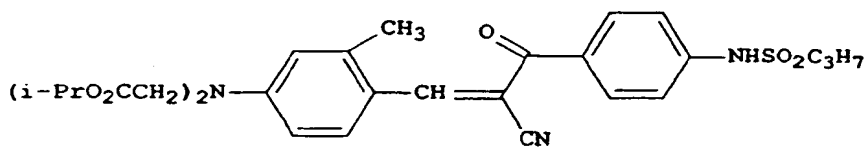
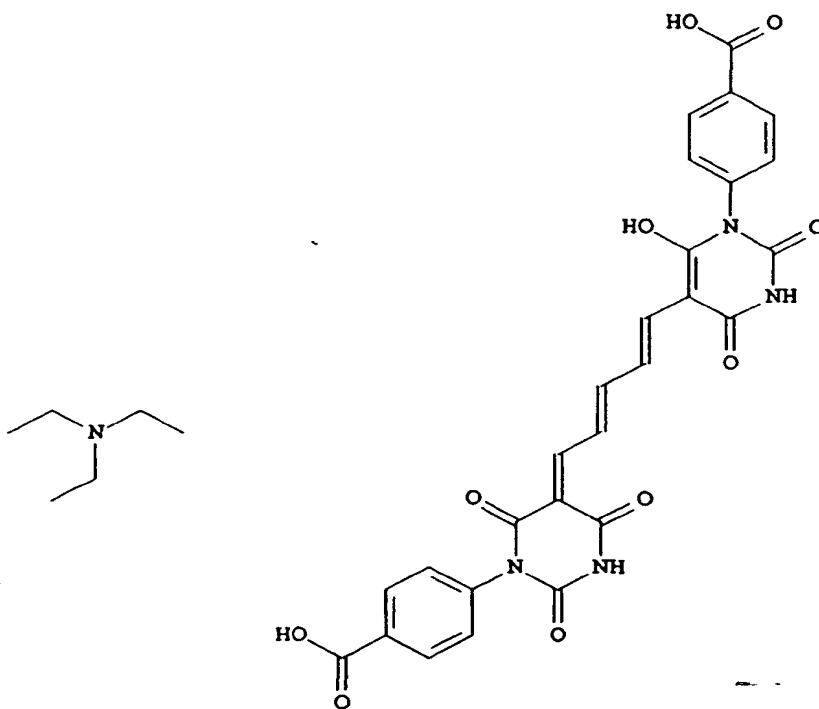
[0024] Preferred dyes of the above formula include those of formula:



where D, X and n are as defined above, and A is an aromatic ring bonded directly or indirectly to D, y is 0 to 4, and X is bonded either on A or an aromatic ring portion of D.

[0025] Exemplary dyes of the above formulas include those in Tables I to X of WO 88/04794, formulas (I) to (VII) of EP 0 456 163 A2, formula (II) of EP 0 594 973, and Tables I to XVI of U.S. Patent 4,940,654. Preferred examples of solid particle filter dyes include the following:

D-1D-2D-3D-4

D-5D-6D-7

[0026] To promote adhesion of the antihalation undercoat to the support, primer layers as hereinabove described are advantageously employed, especially when the support is a polyester support.

[0027] The photographic elements of the present invention can be simple black-and-white or monochrome elements or they can be multilayer and/or multicolor elements.

[0028] Color photographic elements of this invention typically contain dye image-forming units sensitive to each of the three primary regions of the spectrum. Each unit can be comprised of a single silver halide emulsion layer or of multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of

the image-forming units, can be arranged in various orders as is well known in the art.

[0029] A typical multicolor photographic print element in accordance with preferred embodiments of the invention comprises a support bearing, in order, a yellow dye image-forming unit comprising at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler, a cyan dye image-forming unit comprised of at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, and a magenta dye image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler. Each of the cyan, magenta, and yellow image forming units may be comprised of a single light-sensitive layer, a pack of two light-sensitive layers with one being more light sensitive and the other being less light-sensitive, or a pack of three or more light-sensitive layers of varying light-sensitivity.

[0030] The light-sensitive silver halide emulsions employed in the photographic elements of this invention can include coarse, regular or fine grain silver halide crystals or mixtures thereof and can be comprised of such silver halides as silver chloride, silver bromide, silver bromiodide, silver chlorobromide, silver chloriodide, silver chlorobromiodide, and mixtures thereof. The emulsions can be, for example, tabular grain light-sensitive silver halide emulsions. The emulsions can be negative-working or direct positive emulsions. They can form latent images predominantly on the surface of the silver halide grains or in the interior of the silver halide grains. They can be chemically and spectrally sensitized in accordance with usual practices. Photographic print films typically use relatively small grain, high chloride emulsions (e.g., emulsions having average grain size equivalent circular diameters of less than 1 micron and halide contents of greater than 50 mole % chloride) in order to optimize print image quality and enable rapid processing. Such emulsions typically result in relatively low speed photographic elements in comparison to camera negative films. Low speed is compensated for by the use of relatively high intensity print lamps or lasers for exposing such print elements. For comparison purposes, it is noted that motion picture color print films, e.g., when rated using the same international standards criteria used for rating camera negative films, would typically have an ISO speed rating of less than 10, which is several stops slower than the slowest camera negative films in current use. The emulsions typically will be gelatin emulsions although other hydrophilic colloids can be used in accordance with usual practice. The compositions of typical light sensitive image recording layers used in print films are well known, and are not critical to the invention, as any of the silver halide materials used in conventional motion picture films may be used, such as those described, e.g., in Research Disclosure, Item 36544, September, 1994, and the references listed therein.

[0031] The photographic silver halide emulsions utilized in this invention can contain other addenda conventional in the photographic art. Useful addenda are described, for example, in Research Disclosure, Item 36544, September, 1994. Useful addenda include spectral sensitizing dyes, desensitizers, antifoggants, masking couplers, DIR couplers, DIR compounds, antistain agents, image dye stabilizers, absorbing materials such as filter dyes and UV absorbers, light-scattering materials, coating aids, plasticizers and lubricants, and the like.

[0032] Depending upon the dye-image-providing material employed in the photographic element, it can be incorporated in the silver halide emulsion layer or in a separate layer associated with the emulsion layer. The dye-image-providing material can be any of a number known in the art, such as dye-forming couplers, bleachable dyes, dye developers and redox dye-releasers, and the particular one employed will depend on the nature of the element, and the type of image desired.

[0033] Dye-image-providing materials employed with conventional color materials designed for processing with separate solutions are preferably dye-forming couplers; i.e., compounds which couple with oxidized developing agent to form a dye. Preferred couplers which form cyan dye images are phenols and naphthols. Preferred couplers which form magenta dye images are pyrazolones and pyrazolotriazoles. Preferred couplers which form yellow dye images are benzoylacetanilides and pivalylacetanilides.

[0034] In addition to an antihalation undercoat, protective overcoat and backcoat and one or more emulsion layers, the motion picture films of the present invention can contain auxiliary layers conventional in photographic elements, such as primer layers, subbing layers, spacer layers, filter layers, interlayers, pH lowering layers (sometimes referred to as acid layers and neutralizing layers), magnetic recording layers, timing layers, barrier layers and antistatic layers.

[0035] In a particularly preferred embodiment the motion picture films of the invention include an antistatic layer whose antistatic properties survive film processing. The antistatic layers useful in this invention may include a variety of electrically conductive metal-containing particles, such as metal oxides, dispersed in a binder material. Examples of useful electrically conductive metal-containing particles include donor-doped metal oxides, metal oxides containing oxygen deficiencies, and conductive nitrides, carbides, and borides. Specific examples of particularly useful particles include conductive TiO_2 , SnO_2 , V_2O_5 , Al_2O_3 , ZrO_2 , In_2O_3 , ZnO , ZnSb_2O_6 , InSbO_4 , TiB_2 , ZrB_2 , NbB_2 , TaB_2 , CrB , MoB , WB , LaB_6 , ZrN , TiN , WC , HfC , HfN , and ZrC . Examples of the patents describing these electrically conductive particles include; U.S. Patents 4,275,103; 4,394,441; 4,416,963; 4,418,141; 4,431,764; 4,495,276; 4,571,361; 4,999,276; 5,122,445 and 5,368,995. Other useful electrically conductive materials for use in antistatic layers of this invention include:

Semiconductive metal salts such as cuprous iodide as described in U.S. Patents 3,245,833; 3,428,451 and 5,075,171.

Fibrous conductive powders comprising, for example, antimony-doped tin oxide coated onto non-conductive potassium titanate whiskers as described in U.S. Patents 4,845,369 and 5,116,666.

Conductive polymers, such as, the cross-linked vinylbenzyl quaternary ammonium polymers of U.S. Patents 4,070,189, the conductive polyanilines of U.S. Patent 4,237,194, and conductive polythiophenes of U.S. Patent Nos. 4,987,042; 5,035,926; 5,354,613; 5,370,981; 5,372,924; 5,543,944 and 5,766,515.

[0036] A colloidal gel of vanadium pentoxide or silver-doped vanadium pentoxide as described in U.S. Patents 4,203,769; 5,006,451; 5,221,598 and 5,284,714.

[0037] Typically, the antistatic layer is coated at a dry coverage of from 1 to 1000 mg/m² based on total dry weight. The electrical resistivity of the antistatic layer is from 7 to 11 log Ω/\square , preferably from 8 to 11 log Ω/\square , and most preferably from 8.5 to 10 log Ω/\square .

[0038] The antistatic layer may be present on either side or both sides of the support material. The antistatic layer may be an internal layer that underlies the antihalation undercoat, protective overcoat, protective backcoat or the one or more emulsion layers. Alternatively, the antistatic layer may be an outermost layer in which the electrically conductive material is included in the protective overcoat or protective backcoat.

[0039] The antistatic coating formulation may contain a coating aid to improve coatability. The common level of coating aid in the antistatic coating formula is 0.01 to 0.30 weight percent active coating aid based on the total solution weight. However, the preferred level of coating aid is 0.02 to 0.20 weight percent active coating aid based on total solution weight. These coating aids can be either anionic or nonionic coating aids.

[0040] The following examples are intended to illustrate the present invention but not to limit it in scope in any way.

EXAMPLES

[0041] Print film Elements A through H were prepared as follows:

Subbed polyester supports were prepared by first applying a subbing layer comprising a vinylidene chloride copolymer to both sides of a support before drafting and tenting so that the final dried coating weight of the subbing layer was about 90 mg/m².

An antistatic coating was applied onto one side of the support having the following composition:

Acrylonitrile/vinylidene chloride/acrylic acid copolymer binder	2.6 mg/m ²
Electrically-conductive silver-doped vanadium pentoxide fibers	3.3 mg/m ²
Coating surfactant	3.7 mg/m ²

[0042] The antistatic layer had a resistivity of 8.5 log Ω/\square . Protective backcoats having the following general composition were applied onto the antistatic layer for each element:

Sancure 898 polyurethane binder (B.F. Goodrich Corp.)	900 mg/m ²
CX100 polyfunctional aziridine crosslinker (Zeneca Resins)	56 mg/m ²
Coating Surfactant	24 mg/m ²
Michemlube 124 microcrystalline wax (Michelman, Inc.)	12 mg/m ²
NaCl	2.2 mg/m ²
Permanent matte (polymethylmethacrylate beads, avg. size = 1.5 μ m)	See Table 1

[0043] A conventional gelatin subbing layer was applied onto the vinylidene chloride copolymer subbing layer on the side of the support opposite to the antistatic layer and backcoat. Then, an antihalation undercoat having the following composition was applied onto the gelatin subbing layer:

Gelatin	700 mg/m ²
Solid particle dye D-1	53 mg/m ²
Solid particle dye D-7	120 mg/m ²
Coating surfactant	14 mg/m ²
H ₂ SO ₄	5.4 mg/m ²

(continued)

Poly(acrylamide-co-2-acrylamido-2-methylpropane sodium sulfonate)	23 mg/m ²
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[0044] The antihalation undercoat was then overcoated with silver halide emulsion layers suitable for color motion picture print film (a yellow dye image-forming unit comprising a blue-sensitive silver halide emulsion layer having associated therewith a yellow dye-forming coupler, a cyan dye image-forming unit comprised of a red-sensitive silver halide emulsion layer having associated therewith a cyan dye-forming coupler, and a magenta dye image-forming unit comprising a green-sensitive silver halide emulsion layer having associated therewith a magenta dye-forming coupler), and a protective overcoat having the following general composition was applied over the emulsion layers for each element

Deionized gelatin	907 mg/m ²
Polycimethylsiloxane lubricant (Dow Corning)	See Table 1
Permanent matte (polymethylmethacrylate beads, avg. size = 1.5 μ m)	See Table 1
Soluble matte (methylmethacrylate/methacrylic acid 60/40 copolymer beads, avg size = 1.5 μ m)	See Table 1
Charge control surfactant (FT-248 fluorosurfactant, Bayer)	7.5 mg/m ²
Coating surfactant	20 mg/m ²

[0045] The film elements prepared as described above were tested for abrasion resistance in a motion picture projector, ferrotyping resistance, % haze after film processing, soundtrack signal-to-noise ratio, and the number of spot defects in the emulsion layer. Ferrotyping resistance was evaluated by winding 50 foot lengths of each film onto 2 inch diameter plastic cores and keeping the rolls for 3 days at 110F and 60% RH. Films were examined both before and after processing to evaluate ferrotyping resistance, i.e., whether any of the following were observed: sticking together of the roll, significant changes in surface gloss of the emulsion protective overcoat, or any defects in the processed image such as pressure marks as a result of being wound on a core. The samples were rated on a scale of 1 to 5 with 1 being excellent resistance to ferrotyping and 5 being poor resistance to ferrotyping.

[0046] Abrasion resistance in a motion picture projector was evaluated from a continuous loop of processed film sample that had been passed through a motion picture film projector for 100 passes to simulate the normal film life in a movie theater. The tested film was removed from the projector and examined in an optical microscope for abrasion and scratches on the film in the areas where the film surfaces were in contact with the projector. The films were rated on a scale of 1 to 5 with 1 being excellent performance and 5 being poor performance.

[0047] Soundtrack performance was evaluated by printing an analog soundtrack from a sound negative film onto the sample films. The analog sound track was printed in the green light-sensitive layer only of the sample print film within practical exposure levels, and the print film was processed to obtain a silver-plus-magenta dye sound track image. The sample signal-to-noise ratios obtained upon reading with an IR sound track reader are reported in dB, where the higher the number the better the performance in this test.

[0048] The number of spot defects in the film samples were estimated by visual inspection of unprocessed film samples with a 7X magnifying lens.

[0049] The description of the sample elements is given in Table 1 and the results obtained are summarized in Table 2.

TABLE 1.

Sample	Backcoat permanent matte, mg/m ²	Overcoat permanent matte, mg/m ²	Overcoat soluble matte, mg/m ²	Overcoat lubricant level mg/m ²
Element A (Comparative)	25	15	0	15
Element B (Comparative)	25	0	0	45
Element C (Comparative)	25	5	0	45
Element D (Comparative)	25	15	0	45
Element E (Comparative)	25	30	0	15

TABLE 1. (continued)

Sample	Backcoat permanent matte, mg/m ²	Overcoat permanent matte, mg/m ²	Overcoat soluble matte, mg/m ²	Overcoat lubricant level mg/m ²
Element F (Comparative)	2.5	5	150	4.5
Element G (Invention)	2.5	5	15	4.5
Element H (Invention)	5	5	15	4.5

TABLE 2.

Sample	% Haze	Ferrotyping Resistance	Projector Abrasion	Soundtrack Signal-to-Noise	Spot defects
Element A (Comparative)	9.3	1	3	49	none
Element B (Comparative)	5.8	5	1.5	Not tested	none
Element C (Comparative)	6.9	5	1.5	Not tested	none
Element D (Comparative)	8.7	1	1.5	Not tested	none
Element E (Comparative)	11.8	1	Not tested	Not tested	none
Element F (Comparative)	Not tested	1	1	Not tested	many
Element G (Invention)	4.2	1	1	51	trace
Element H (Invention)	4.7	1	1	Not tested	trace

[0050] The results presented in Table 2 show that only Elements G and H of the invention provide excellent performance in all the tests. The Comparative Elements give poorer performance in one or more of the tests.

Claims

1. An unprocessed motion picture print film photographic element comprising a support having on one side thereof at least one silver halide emulsion layer and an outermost protective overcoat layer comprising a film-forming binder, and having on the opposite side thereof an outermost protective backcoat layer comprising a film-forming binder; wherein

the protective overcoat and backcoat layers each comprise at least 1 mg/m² of permanent matting agent having an average size of from 0.5 to 3 micrometers,
the total permanent matting agent amount in the overcoat and backcoat layers combined is less than 25 mg/m²,
at least one of the overcoat or backcoat layers comprises soluble matting agent having an average size of from 0.5 to 3 micron which is removed upon photographic processing, and
the total soluble matte amount in the overcoat and backcoat layers combined is from 2.5 to 30 mg/m².

2. An element according to claim 1, further comprising an antihalation undercoat between the support and the silver halide emulsion layer.
3. An element according to claim 1 or 2, further comprising an antistatic layer on either side of the support.

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4. An element according to claim 3, wherein the antistatic layer is coated between the support and the outermost backcoat layer.

5. An element according to any of claims 1-4, wherein the film forming binder for the outermost backcoat comprises an aliphatic polyurethane.

6. An element according to any of claims 1-5, wherein the soluble matting agent in at least one of the overcoat or backcoat layers is present at a level at least equal to that of the permanent matting agent.

7. An element according to any of claims 1-6, comprising a support bearing, in order, a yellow dye image-forming unit comprising at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler, a cyan dye image-forming unit comprised of at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, and a magenta dye image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 00 20 4679

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Y	EP 0 567 118 A (FUJI) 27 October 1993 (1993-10-27) * page 9, line 23 - line 35 * * page 19, line 4 - line 7 * * page 20, line 6 - line 7 * * page 23; table 1 * * page 29, line 31 - line 36 * * page 31; table 2 *	1-7	G03C1/76 G03C7/30
Y	EP 0 772 080 A (KODAK) 7 May 1997 (1997-05-07) * page 2, line 41 - line 45 * * page 4, line 4 - line 10 * * page 7, line 23 - line 24 * * page 8, line 2 - line 16 * * page 9, line 47 - line 49 *	1-7	
D	& US 5 679 505 A 21 October 1997 (1997-10-21)		
A	US 5 952 165 A (ANDERSON ET AL.) 14 September 1999 (1999-09-14) * column 2, line 17 - line 27 * * column 5, line 22 - line 32 * * column 5, line 41 - line 47 * * column 7, line 30 - line 32 * * column 8, line 5 - line 11 * * column 10, line 30 - line 42 * * column 10, line 54 - line 56 *	1-7	TECHNICAL FIELDS SEARCHED (Int.Cl.7) G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22 January 2001	Examiner Magrizos, S
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 20 4679

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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22-01-2001

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 567118	A	27-10-1993	JP 2811256 B	15-10-1998
			JP 5297505 A	12-11-1993
			DE 69321024 D	22-10-1998
			DE 69321024 T	08-04-1999
			US 5342733 A	30-08-1994
EP 772080	A	07-05-1997	US 5679505 A	21-10-1997
			DE 69602904 D	22-07-1999
			DE 69602904 T	04-11-1999
			JP 9171228 A	30-06-1997
US 5952165	A	14-09-1999	EP 0962816 A	08-12-1999
			JP 2000010240 A	14-01-2000

EPO FORM P4495

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82